A11102 128985

NAT'L INST OF STANDARDS & TECH R.I.C.

A11102128985

/Bureau of Standards journal of research
QC1 .U52 V8;1932 C.1 NBS-PUB-C 1928

VOLUMETRIC DETERMINATION OF PENTOSES AND PENTOSANS [1]

By G. M. Kline and S. F. Acree

ABSTRACT

The determination of pentoses and pentosans involves two steps, namely, distillation of the sample with 12 per cent hydrochloric acid and estimation of the furfural in the distillate. It was found that steam distillation did not give any better yields of furfural from xylose than the standard method of distillation. Gravimetric and volumetric procedures for determining the distilled furfural were studied with particular reference to the excess bromine titration method of Powell and Whittaker. The latter method has the advantages of speed and accuracy over wide ranges of concentration. The effects of various chemical substances and experimental conditions on the yield of furfural were investigated. The loss of furfural due to the presence of nitric acid in the distillation mixture was reduced by precipitation of the nitrates with nitron.

CONTENTS

	Page
I. Introduction	25
II. Experimental work	27
1. Effect of distillation method on furfural yield	27
2. Relative accuracy of gravimetric and volumetric methods for determining furfural	29
3. Rate of distillation of furfural from a xylose-hydrochloric acid mixture by steam	32
4. Effect of various chemical substances on the yield of furfural	32
5. Effect of exposure to air on loss of furfural	34
6. Effect of washing furfuralmalonylthiourea precipitate with water and hydrochloric acid	34
III. Discussion of results	35
IV. Summary and conclusions	35

I. INTRODUCTION

The "standard" method for the determination of pentosans is distillation of the sample with 12 per cent hydrochloric acid and precipitation of the resultant furfural with phloroglucinol.[2] This method has many disadvantages: (1) It is empirical; (2) experimental conditions, such as concentration of carbohydrate and acid, and rate of distillation must be carefully controlled; (3) it is time-consuming; (4) an artificial set of corrections must be applied; and (5) it is lacking in accuracy.

Considerable investigation has been devoted in recent years to finding a better method, particularly with regard to the estimation of

Read in part at the Buffalo meeting of the American Chemical Society, September, 1931.

[1] Acknowledgement is made of the contributions of W. L. Hall, G. W. Irving, W. Seaton, C. S. Slater, and B. Wingfield to the studies described in this paper.

[2] Official and Tentative Methods, Association of Official Agricultural Chemists, p. 120; 1925.

the distilled furfural. The procedure that seems to have met with the most favor is the thiobarbituric acid method of Dox and Plaisance.[3] This method, however, like that employing phloroglucinol, is a precipitation procedure and has many of the disadvantages of the "standard" method. Sweeney [4] concludes that "from the standpoint of difficulties encountered in the manipulation of the determinations the methods are about equal." It will be shown in this paper that the use of thiobarbituric acid has the disadvantage that very small quantities of furfural can not be determined accurately. The phloroglucinol method also becomes less accurate for small amounts of furfural.

Several volumetric methods have been proposed for the determination of furfural distilled from pentosans. Pervier and Gortner [5] have published a review of the earlier proposals. These authors also describe a method involving the titration of furfural in acidified potassium bromide solution with potassium bromate. The reagent is added slowly from a burette until free bromine persists in the solution as indicated electrometrically. Under these conditions 1 molecule of bromine reacts with 1 molecule of furfural. However, there is a tendency for the oxidation product to react further with bromine, and subsequent workers have found great difficulty in determining the end point by the above procedure.

The use of an excess of bromine to react with the furfural and titration of the unused bromine has been proposed by Van Eck [6] and Powell and Whittaker.[7] This method, as described by the latter authors, has the advantage that the analysis can be completed in a single day instead of the two to three days required by the precipitation methods. In fact, after the distillation of the furfural is completed, the analysis can be finished in a little more than an hour by the volumetric procedure, whereas the precipitation methods require that the precipitate be allowed to stand overnight before filtering, and further that the precipitate be dried at 105° for from four hours to overnight before weighing. Powell and Whittaker have found very good agreement in the results of pentosan determinations made on wood cellulose by their bromine method and the standard phloroglucinol method. Schorger [8] has included a description of this method in his book, "The Chemistry of Cellulose and Wood." Three recent articles [9] have appeared in foreign journals recommending the use of this method or modifications of it, but no study or application of it has been published in this country.

The standard method [10] for distillation of samples containing pentoses or pentosans prescribes the addition of 100 ml of 12 per cent hydrochloric acid to the material in a 250 ml flask and distillation at the rate of 30 ml in 10 minutes. As soon as 30 ml of distillate are collected, a like amount of the 12 per cent hydrochloric acid is added

---

[3] Dox, A. W., and Plaisance, G. P. J. Am. Chem. Soc., vol. 38, p. 2156; 1916. Wise, L. E., and Peterson, F. C. Ind. Eng. Chem., vol. 22, p. 362; 1930. Hansen, L. P., Paper presented before the sugar division at the Cincinnati meeting of the American Chemical Society; September, 1930.

[4] Sweeney, O. R. Bulletin 73, Iowa Engineering Experiment Station.

[5] Pervier, N. C., and Gortner, R. A., Ind. Eng. Chem., vol. 15, p. 1255; 1923.

[6] Van Eck, P. N., Versl. v. d. Verricht. v. h. centr. lab. v. d. Volksgezondh.; 1918. Chem. Abstr., vol. 14, p. 509; 1920.

[7] Powell, W. J. and Whittaker, H., J. Soc. Chem. Ind., vol. 43, p. 35T; 1924.

[8] Schorger, A. W., The Chemistry of Cellulose and Wood; 1926.

[9] Kullgren, C., and Tyden, H., Ing. Vetenskaps Akad. Handl.; 1929, No. 94, pp. 3–62. Chem. Abstr., vol. 24, p. 1316; 1930. Deshpande, D. D., J. Indian Inst. Sci., vol. 13A, p. 110; 1930. Sasaki, K., J. Agr. Chem. Soc. Japan, vol. 6, p. 538; 1930, Chem. Abstr., vol. 24, p. 5670; 1930.

[10] See footnote 2, p. 25.

to the flask through a separatory funnel; the distillation is continued in this manner until 360 ml of distillate are collected. This procedure has been criticized on the grounds that the furfural is decomposed by the concentrated hydrochloric acid vapors. The use of steam distillation has been suggested by Jolles [11] and Pervier and Gortner, and practically quantitative results reported. The avoidance of destruction of furfural has been assumed to be due to the low acidity of the distillate and to the prompt removal of the furfural by the current of steam.

This paper presents the results of a study of the standard and steam distillation procedures, a comparison of volumetric bromine methods and the gravimetric thiobarbituric acid method for determining furfural, and the effect of various conditions and substances on the yield of furfural.

II. EXPERIMENTAL WORK

1. EFFECT OF DISTILLATION METHOD ON FURFURAL YIELD

In order to determine the relative efficiency of the standard and steam distillation methods similar aliquots of a solution of xylose were distilled by the two procedures.

(a) STANDARD METHOD OF DISTILLATION

The method of the Association of Official Agricultural Chemists was used. The sample is placed in a 250 ml flask and 100 ml of 12 per cent hydrochloric acid (specific gravity 1.06) are added. Distillation is conducted at the rate of 30 ml in 10 minutes. The distillate is passed into the receiver through a small filter. As soon as 30 ml of distillate are collected, 30 ml of 12 per cent hydrochloric acid are added to the flask. Distillation is continued in this manner until 360 ml of solution have been collected.

(b) STEAM DISTILLATION METHOD

The steam distillation method was used as proposed by Pervier and Gortner except that the temperature of distillation rose to about 108° instead of the 103° to 105° recommended by these authors. They found, however, that theoretical results were also obtained by steam distillation at temperatures of 107° to 108°. The weighed sample and 200 ml of 12 per cent hydrochloric acid are placed in a 750 ml flask fitted up for steam distillation. A slow current of steam is conducted into the mixture and as soon as the boiling temperature is reached, the distilling flask is heated with a low flame. Distillation is continued until the distillate no longer gives a red coloration with aniline acetate test paper.

The distillation of 0.0697 g of xylose by each of these methods yielded practically equal amounts of furfural. Table 1 shows that the percentage of xylose recovered as furfural was not the theoretical value, but only about 88 to 92 per cent of the total. These two experiments indicate that the destruction or loss of furfural is not avoided by using steam distillation.

Further evidence that the standard and steam distillation methods give about the same yield of furfural is afforded by the data presented in Table 2. The distillation of 0.03 to 0.5 g xylose gives an amount

[11] Jolles, A., Sitz. Akad. Wiss. Wien, vol. 114, Abt. II, p. 1191; 1905.

of furfural equivalent to 73 to 88 per cent of the xylose as determined by precipitation of the furfural with thiobarbituric acid. Similar results were obtained by two different investigators in this laboratory. These values are more nearly in agreement with the yields of xylose resulting from distillation according to the standard procedure and precipitation with phloroglucinol as found by Krober than with the theoretical yields reported by Pervier and Gortner. It would appear, therefore, that steam distillation does not materially improve the yield, and that further work is needed upon this problem of obtaining theoretical yields of furfural from xylose.

TABLE 1.—*Comparison of the "standard" and steam distillation methods for converting xylose to furfural*

Weight of xylose	Method of distillation	Yield of furfural		Xylose recovered	
		Thiobarbituric acid method	Excess bromine method	Thiobarbituric acid method	Excess bromine method
g		*g*	*g*	*Per cent*	*Per cent*
0.0697	Standard	0.0392	0.0412	88.02	92.35
.0697	Steam	.0392	.0410	88.02	91.93

TABLE 2.—*Estimation of xylose by gravimetric and volumetric determination of the distilled furfural*

[Samples of pure xylose were steam distilled with 12 per cent hydrochloric acid. The distillate was made up to 500 ml and 200 ml aliquots taken for each determination. Data are expressed as total recovery]

Weight of xylose	Xylose found	
	Precipitation with thiobarbituric acid	Bromine titration
g	*Per cent*	*Per cent*
[1] 0.0127	51.63	----------
.0139	29.10	93.53
[1] .0346	73.00	----------
[1] .0662	74.15	----------
.0697	88.02	91.93
.1393	83.05	85.06
[1] .1673	83.60	----------
.2786	83.29	81.52
[1] .3376	83.40	----------
[1] .5060	81.85	----------

[1] These experiments were performed by Baker Wingfield.

TABLE 3.—*Recovery of furfural by distillation*

Weight of furfural	Method of distillation	Method of analysis of distillate	Amount of furfural recovered	Furfural recovered
g			*g*	*Per cent*
[1] 0.1200	Steam	Electrometric-bromate titration	0.1195	99.58
[1] .1200	do	do	.1195	99.58
[1] .1200	do	do	.1154	96.17
[2] .1062	Standard	Thiobarbituric-acid precipitation	.1054	99.25
[2] .1062	do	do	.1048	98.68

[1] These experiments were performed by C. S. Slater.
[2] These samples were added to the residual liquors from the distillation of 3 g portions of peanut shells with 12 per cent hydrochloric acid. The experiments were performed by W. L. Hall.

The data in Table 3 indicate that furfural itself can be recovered with slight losses by distillation with 12 per cent hydrochloric acid either by the standard procedure or with steam. Two of the distillations were carried out in the presence of other organic substances, such as lignin and cellulose present in peanut hulls. The failure to recover an amount of furfural equivalent to the pentoses or pentosans present is, therefore, not due to a destructive action of concentrated hydrochloric acid on furfural, but rather to another reaction of the pentose material during conversion into furfural.

2. RELATIVE ACCURACY OF GRAVIMETRIC AND VOLUMETRIC METHODS FOR DETERMINING FURFURAL

In the course of analysis of extracts of wheat straw, cottonseed hull bran, and samples of xylose, data were obtained on the yields of furfural as indicated by the thiobarbituric acid method and the bromine titration methods of Pervier and Gortner and of Powell and Whittaker on duplicate aliquots of various distillates. The data are given in Table 4.

TABLE 4.—*Comparison of the thiobarbituric acid and bromine methods for the determination of furfural*

[Samples of straw extracts, cottonseed hull bran and xylose were steam distilled with 12 per cent HCl. The distillate was made up to 500 ml and 200 ml aliquots were taken for each determination. Data for xylose are given as the amount of furfural theoretically present and actually recovered in the aliquot analyzed]

Sample	Furfural recovered		
	Thiobarbituric-acid method	Excess-bromine method	Electrometric-bromate titration method
	g	*g*	
1. Straw extract	0.0000	0.0019	
2. Xylose—0.0036 g furfural	.0010	.0033	
3. Straw extract	.0000	.0037	
4. Straw extract	.0060	.0075	
5. Straw extract	.0074	.0097	
6. Straw extract	.0133	.0146	
7. Xylose—0.0178 g furfural	.0157	.0164	
8. Straw extract	.0196	.0194	
9. Straw extract	.0241	.0245	
10. Xylose—0.0357 g furfural	.0296	.0303	
11. Xylose—0.0713 g furfural	.0594	.0581	
12. Cottonseed-hull bran extract	[1] .0573		[2] 0.0557
13. Furfural: 1173 g	[1] .1169		[2] .1178

[1] These determinations were made by W. L. Hall.
[2] These determinations were made by C. S. Slater.

(a) THIOBARBITURIC-ACID METHOD

The procedure used was that of Dox and Plaisance described in Sweeney's bulletin on The Commercial Utilization of Corncobs. Exactly 0.9 g of thiobarbituric acid is ground in an agate mortar with just enough water to moisten it. The ground paste is washed into a beaker and made up to 150 ml. After the acid has gone into solution, 75 ml of hydrochloric acid, specific gravity 1.06, are added slowly, with stirring. The solution is filtered through asbestos and is ready for use. For the precipitation, the solution (aliquot) of furfural is made up to 12 per cent hydrochloric acid and treated with twice the theoretical amount of the fresh thiobarbituric acid. The precipitate

which forms is allowed to stand for 24 hours. It is then filtered through a Gooch crucible, washed and dried overnight at 100° C. One gram of the condensation product contains 0.4323 g furfural.

(b) ELECTROMETRIC BROMATE TITRATION METHOD

The proposed method of Pervier and Gortner was followed. To the solution containing furfural 5 ml of 20 per cent potassium bromide are added for every 100 ml of solution and the acidity (HCl) is adjusted to about 4 per cent by weight. With continual stirring $N/10$ potassium bromate solution is run in slowly from a burette until the pale yellow color of bromine persists for a short period. At this point the bromate is added in small increments and the time is recorded which is required for the disappearance of free bromine as indicated by the use of a sensitive galvanometric set-up. As the end point is crossed a rather large increase in the time required will be noted. The number of milliliters of $N/10$ potassium bromate required multiplied by 0.004803 gives the number of grams of furfural in the sample. In this titration 1 molecule of bromine reacts with 1 molecule of furfural.

(c) EXCESS BROMINE METHOD

The procedure recommended by Powell and Whittaker was followed. To make up the standard bromide-bromate solution dissolve 3 g of potassium bromate and 50 g of potassium bromide in distilled water and dilute to 1 liter. The distillate of furfural is made up to 500 ml with 12 per cent hydrochloric acid. Then 25 ml portions of the bromate-bromide reagent are pipetted into glass-stoppered flasks and 200 ml aliquots of the distillate are added to each flask. Also 200 ml of the 12 per cent hydrochloric acid are added to one of the flasks, containing 25 ml of the reagent to serve as a blank. The bottles are allowed to stand in the dark for one hour, and after the addition of 10 ml of 10 per cent potassium iodide solution, the liberated iodine is determined by titration with $N/10$ sodium thiosulphate. The number of milliliters of $N/10$ thiosulphate required by the sample is subtracted from the number of milliliters required by the blank, the difference being a measure of the furfural present. One milliliter of $N/10$ sodium thiosulphate is equivalent to 0.0024 g of furfural. In this method 2 molecules of bromine react with 1 molecule of furfural.

The data in Table 4 show that for amounts of furfural less than 0.01 g the precipitation method gives low results. For very small amounts of furfural, 0.002 to 0.003 g, such as may be obtained from wood cellulose, dilute extracts of raw-plant substances, and materials containing small quantities of pentoses and pentosans as impurities, the precipitation method either fails to indicate the presence of any furfural or precipitates only a small fraction thereof. The excess bromine titration method, however, is sensitive to these small amounts of furfural. Finally the electrometric bromate titration method of Pervier and Gortner gave values in experiments in Tables 3 and 4 with amounts of furfural between 0.05 and 0.12 g which were comparable with the results of analysis with thiobarbituric acid. The data in Table 5 and experiments 3 and 4, Table 6, show, however, that accurate results with small quantities are difficult to obtain with this method. The end point is indefinite due to a second reaction involving the combination of another molecule of bromine with furfural. The method of Powell and Whittaker in which an excess of bromine

is allowed to react with the furfural gives a satisfactory end point. In view of the advantageous combination of speed and accuracy in the excess bromine titration method for determining furfural distilled from pentoses and pentosans as indicated by the published work of Powell and Whittaker, Deshpande and Sasaki, and by the data presented in this paper, it is believed to be worthy of consideration as an official method.

TABLE 5.—*Determination of furfural by electrometric bromate titration* [1]

Weight of furfural taken	Volume of $NaBrO_3$ consumed	Weight of furfural found
g	*ml*	*g*
0.060	12.20	0.0591
.060	12.49	.0605
.060	12.50	.0605
.060	12.60	.0610
.060	12.65	.0612
.060	12.80	.0620
.067	13.45	.0651
.078	15.80	.0765
.1173	24.34	.1178

[1] The experimental data presented in this table were obtained by C. S. Slater.

TABLE 6.—*Rate of distillation of furfural from a xylose-hydrochloric acid mixture by steam*

Experiment No.	Weight of xylose taken	Sample	Weight of furfural found	Weight of xylose found
	g		*g*	*g*
1 [1]	0.0697	First 50 ml	0.0057	0.0089
		Second 50 ml	.0085	.0133
		Third 50 ml	.0089	.0140
		Fourth 50 ml	.0093	.0146
		Fifth 50 ml	.0061	.0095
		Sixth 50 ml	.0027	.0042
		Seventh 50 ml.[3]	.0009	.0014
		Eighth 50 ml.[3]	.0005	.0007
		Total	.0426	.0666
2 [1]	.0697	400 ml	.0410	.0641
3 [2]	.1500	First 50 ml	.0336	.0525
		Second 50 ml	.0305	.0477
		Third 50 ml	.0121	.0189
		Fourth 50 ml	.0068	.0106
		Fifth 50 ml	.0019	.0030
		Sixth 50 ml	.0010	.0016
		Total	.0859	.1343
4 [2]	.1500	300 ml	.0905	.1414

[1] The determination of furfural in these experiments was made by the excess-bromine method. In experiment 2 the titration was carried out with a 2/5 aliquot.

[2] The determination of furfural in these experiments was made by C. S. Slater using the electrometric-bromate titration method.

[3] 50 ml of 12 per cent hydrocloric acid were added to the mixture in the distilling flask after 300 and 350 ml, respectively, of distillate had been collected.

Titration of the furfural with iodine and alkali according to the method recently recommended for aldehydic sugars [12] was also attempted. The furfural, however, reacted more slowly with these reagents than did the sugars, and therefore most of the iodine was converted to iodate rather than consumed in the oxidation of the furfural. Higher temperatures and longer time periods did not materially affect the results obtained. These observations confirm the

[12] Kline, G. M., and Acree, S. F., Analytical ed., Ind. and Eng. Chem., vol. 2, p. 413; 1930. B. S. Jour. Research, vol. 5, p. 1063; 1930.

negative results obtained by Pervier and Gortner with sodium hypoiodite.

3. RATE OF DISTILLATION OF FURFURAL FROM A XYLOSE-HYDROCHLORIC ACID MIXTURE BY STEAM

The official method of distillation is assumed to give all of the potential furfural in 360 ml distillate. Using steam distillation Pervier and Gortner collected an average of 800 ml; moreover, with 0.2 g samples of xylose volumes of distillate varying from 300 to 1,000 ml apparently gave quantitative recoveries of the sugar as furfural. Experiments on the rate of distillation of furfural are presented in Table 6. The amount of furfural distilling over fell off rapidly after 200 ml had been collected. The amount of furfural present in any 50 ml portion in experiment 1 was less than 0.01 g. In view of the results of the experiments in Table 4, it is readily seen that the precipitation method would not have been practical for estimating such small amounts of furfural. Therefore, with a more sensitive method, such as was used in these experiments for determining furfural, it may be found that the usual practice of collecting 360 ml of distillate does not obtain all the furfural that it is possible to distill from the pentoses or pentosans.

4. EFFECT OF VARIOUS CHEMICAL SUBSTANCES ON THE YIELD OF FURFURAL

It has been noted in a previous article [13] that the presence of nitric acid results in a lowered yield of furfural. These conditions are encountered particularly in extracts made with nitric acid or in nitrated materials. Table 7 shows the effect of increasing amounts of nitrates on the yield of furfural. In the presence of large amounts of nitrates (1.5 g KNO_3) the effect of the hydrochloric-nitric acid mixture is such that no furfural at all is found in the distillate. The nitric acid may act directly on the xylose as discussed in another article,[14] or it may oxidize the furfural. The last two experiments in Table 7 indicate that the nitric acid or possibly chlorine acts upon the furfural rather than on the pentose or pentosan.

To overcome this action of nitric acid the effect of the addition of various reducing agents to xylose and xylose-nitrate mixtures was studied. The results are presented in Table 8. Stannous chloride in 5 g amounts caused lower yields of furfural than the 0.1675 g KNO_3. Sulphurous acid, ferrous sulphate, and ferrous ammonium sulphate did not materially affect the yield of furfural from xylose, but they also had very little effect in decreasing the loss of furfural due to action of the nitric acid. The addition of small amounts of hydrazine sulphate and urea to xylose-nitrate-ferrous ammonium sulphate mixtures resulted in smaller yields of furfural. Removal of the nitrates by precipitation with nitron and filtration gave much better yields of furfural. Nitron itself had only a slight effect on the yield of furfural from xylose alone. It is therefore recommended that in determining the pentosan content of nitrate-containing materials preliminary treatment with nitron be carried out before liberating furfural.

---

[13] Hall, W. L., Slater, C. S., and Acree, S. F., B. S. Jour. Research, vol. 4, p. 329; 1930.
[14] Kline, G. M., and Acree, S. F., Ind. & Eng. Chem., vol. 22, p. 975; 1930.

TABLE 7.—*Effect of varying amounts of nitrates on furfural yield* [1]

[All samples made up to 100 ml volume and 12 per cent HCl and distilled by standard procedure. Furfural determined by thiobarbituric acid precipitation method]

No. of experiment	Sample	Weight thiobarbituric acid precipitate	Equivalent weight of furfural	Equivalent weight of xylose	Xylose recovered	Xylose found using Krober's table
		g	*g*	*g*	*Per cent*	*Per cent*
I 1	0.2003 g xylose	0.2570	0.1111	0.1736	86.69	97.65
I 2	do	.2590	.1120	.1750	87.37	98.50
I 3	0.2003 g xylose+0.0125 g KNO_3	.2484	.1073	.1678	83.79	94.26
I 4	do	.2540	.1098	.1716	85.68	96.51
I 5	0.2003 g xylose+0.0250 g KNO_3	.2470	.1068	.1669	83.32	93.81
I 6	do	.2467	.1067	.1667	83.22	93.76
S 7	0.2003 g xylose+0.0300 g KNO_3	.2501	.1081	.1690	84.36	95.01
I 8	0.2003 g xylose+0.0500 g KNO_3	.2242	.0969	.1515	75.63	85.17
I 9	do	.2280	.0986	.1540	76.91	86.67
S 10	0.2003 g xylose+0.0625 g KNO_3	.2154	.0931	.1455	72.66	81.83
I 11	0.2003 g xylose+0.0875 g KNO_3	.1860	.0804	.1257	62.74	70.74
I 12	do	.1936	.0837	.1308	65.31	73.59
I 13	0.2003 g xylose+0.1250 g KNO_3	.1751	.0757	.1183	59.07	66.55
I 14	do	.1773	.0767	.1198	59.81	67.45
I 15	0.2003 g xylose+0.1675 g KNO_3	.1510	.0653	.1020	50.94	57.46
S 16	do	.1536	.0664	.1038	51.81	58.46
S 17	0.2003 g xylose+1.5000 g KNO_3	None.				
H 18	0.1173 g furfural+0.1250 g KNO_3	.1738	.0751		[2] 64.05	
H 19	do	.1732	.0749		[2] 63.83	

[1] The experiments in this table were performed by W. L. Hall, G. W. Irving, and W. Seaton.
[2] Per cent furfural recovered.

TABLE 8.—*Effect of various substances on the loss of furfural due to nitrates* [1]

All samples made up to 100 ml volume and 12 per cent HCl concentration, and distilled by standard procedure. Furfural determined by thiobarbituric acid precipitation method]

No. of experiment	Sample	Weight thiobarbituric acid precipitate	Equivalent weight of furfural	Equivalent weight of xylose	Xylose recovered	Xylose found using Krober's table
		g	*g*	*g*	*Per cent*	*Per cent*
S 1	0.2003 g xylose+0.1675 g KNO_3+5 g $SnCl_2 \cdot 2H_2O$.	0.1431	0.0619	0.0967	48.27	54.47
S 2	0.2003 g xylose+5 g $SnCl_2 \cdot 2H_2O$	.1372	.0593	.0927	46.28	52.22
S 3	0.2003 g xylose+0.1250 g KNO_3+1.5 g H_2SO_3.	.1812	.0783	.1224	61.12	68.85
S 4	0.2003 g xylose+1.5 g H_2SO_3	.2627	.1136	.1775	88.61	99.85
S 5	0.2003 g xylose+0.1675 g KNO_3+25 g $FeSO_4 \cdot 7H_2O$.	.1861	.0805	.1257	62.78	70.84
S 6	0.2003 g xylose+25 g $FeSO_4 \cdot 7H_2O$	.2482	.1073	.1677	83.72	94.26
S 7	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.	.2145	.0927	.1449	72.36	81.48
I 8	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.[2]	.1634	.0706	.1104	55.12	62.11
I 9	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.[2]	.1447	.0626	.0978	48.81	55.17
S 10	0.2003 g xylose+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.	.2584	.1117	.1746	87.16	98.20
I 11	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$+0.5 g hydrazine sulphate.	.1959	.0847	.1324	66.08	74.49
I 12	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$+0.25 g urea.	.2033	.0879	.1374	68.58	77.28
I 13	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$+0.50 g urea.	.1825	.0789	.1233	61.56	69.40
I 14	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$+1.0 g urea.	.1715	.0741	.1159	57.85	65.20
I 15	0.2003 g xylose+0.1250 g KNO_3+1 g nitron [2] [3]	.2336	.1010	.1578	78.80	88.77
I 16	0.2003 g xylose+0.1250 g KNO_3+1 g nitron [2] [3].	.2160	.0934	.1459	72.86	82.13
I 17	0.2003 g xylose+0.5 g nitron	.2565	.1109	.1733	86.52	97.45
I 18	0.2003 g xylose+0.5 g nitron	.2579	.1115	.1742	86.99	98.00

[1] The experiments in this table were performed by G. W. Irving and W. Seaton.
[2] Solution filtered before making up to 12 per cent HCl and distilling.
[3] Precipitate of nitron-nitrate equivalent to 0.1234 g out of 0.1250 g KNO_3.

TABLE 9.—*Loss of furfural on exposure to air* [1]

Sample	Time exposed	Amount furfural originally present	Volume of $NaBrO_3$ consumed	Amount furfural found
		g	*ml*	*g*
10 ml 0.6 per cent furfural solution, 10 ml 8 per cent HCl and 1 ml 20 per cent KBr	40 minutes	0.060	10.30	0.0499
10 ml 0.6 per cent furfural solution, 10 ml 8 per cent HCl	50 minutes	.060	10.25	.0496
10 ml 0.6 per cent furfural solution	65 minutes	.060	8.5	.0411
	16 hours	.060	0.5	.0024
	do	.060	0.4	.0019

[1] These experiments were performed by C. S. Slater.

5. EFFECT OF EXPOSURE TO AIR ON LOSS OF FURFURAL

In a few experiments in which several samples of furfural solutions were prepared at one time and analyzed in succession by the electrometric bromate titration method, a decreasing yield of furfural was noted. Inasmuch as the flasks had been open to the air, loss due to volatilization of furfural was suspected. A series of experiments in which the furfural solutions were left exposed to the air for varying lengths of time before analysis is presented in Table 9. These experiments show that after 16 hours very little furfural remains in the solution. It would seem that some protection of the distillate from exposure to air during the two hours required for completion of the distillation would be advisable. The filtration device used by us in the mouth of the graduate cylinder receiving the distillate was a folded filter inside a funnel with a cover of paper or glass containing a hole through which the condenser passed. This arrangement probably prevents evaporation to a large extent by protecting the distillate from air currents inasmuch as the yields of furfural from pure solutions of furfural are nearly quantitative. However, in the present standard apparatus, the distillate is largely unprotected from the time it reaches the end of the condenser open to the air until it passes through the filter paper.

6. EFFECT OF WASHING FURFURALMALONYLTHIOUREA PRECIPITATE WITH WATER AND HYDROCHLORIC ACID [15]

In the experimental determination of furfural by precipitation with thiobarbituric acid, it was found that when the filtered precipitate is excessively washed with distilled water a cloudiness appears stratified upon the first filtrate. This cloudiness was found also, though to a lesser degree, when washings were made with 3 and 6 per cent hydrochloric acid. Washing with 12 per cent hydrochloric acid gave no cloudiness. However, washings with 12 per cent hydrochloric acid on standing showed a slight sediment in the bottom of the flask. This sediment was also found when the precipitating reagent (acidified thiobarbituric acid) was made up to the same concentration of hydrochloric acid as would be found in the filtrate. The sediment in the second case is therefore not the furfuralmalonylthiourea, but comes from the thiobarbituric acid. Washing a weighted amount of the dried furfural precipitate with water and hydrochloric acid showed slight losses for both, but in this experiment the precipitates are not in the same physical condition as those obtained in carrying

[15] This experimental work on washing the precipitate was performed by W. L. Hall.

out the analysis. If some of the furfuralmalonylthiourea is shaken up in water and allowed to become saturated overnight and then filtered, the filtrate is slightly cloudy. Colloidal particles can be seen with the ultramicroscope. Addition of 12 per cent hydrochloric acid to the filtrate causes the colloidal particles to settle out. From this it seems evident that washing the fresh precipitate with water causes the formation of a colloidal solution whereas the use of 12 per cent hydrochloric acid prevents it. It is therefore recommended that the excess thiobarbituric acid reagent be removed from the precipitate by washing with 12 per cent hydrochloric acid rather than with water.

III. DISCUSSION OF RESULTS

A number of workers have tried the method of Pervier and Gortner with its indefinite end point, and, finding it tedious and difficult to obtain consistent results, have abandoned the bromine method altogether. Our studies have shown that by using an excess of bromine to react with the furfural and determining the bromine left by the use of potassium iodide and thiosulphate solutions we can make the furfural determination quickly and accurately. Although the method has been said to have the disadvantage that no corrections can be applied for hydroxymethyl-furfural, methylfurfural, and oxidizable impurities that may be obtained in appreciable quantities from raw plant substances, the results obtained for wood pulp and purified wood by Powell and Whittaker and for straw extracts by our experiments show good agreement between the volumetric and precipitation procedures. The great saving, both in personal attention required and in the time elapsing before the results can be reported should stimulate a further study of this volumetric procedure.

IV. SUMMARY AND CONCLUSIONS

The results of a study of the standard and steam distillation procedures for the formation and separation of furfural from xylose, a comparison of the volumetric bromine methods and the gravimetric thiobarbituric acid method for determining furfural, and the effect of various chemical substances and experimental conditions on the yield of furfural are presented in this paper.

Steam distillation did not give any better yields of furfural from xylose than the standard method of distillation.

The excess bromine titration method for determining furfural distilled from pentoses and pentosans has the advantages of speed and accuracy over wide ranges of concentration. It is suggested that this method is worthy of consideration as an official method.

The presence of nitric acid or nitrates in the distillation mixture causes the destruction of furfural. This loss can be greatly reduced by preliminary removal of the nitrates with nitron.

It is felt that the phase of this subject needing most attention at this time is the study of the best conditions for the conversion of the pentose or pentosan into practically 100 per cent of furfural. The yields are too low and variable at present.

Washington, June 30, 1931.